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METHOD FOR PRODUCTION  
THEREOF

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**SUBMISSION OF CERTIFIED PRIORITY DOCUMENT**

Enclosed herewith is a certified copy of European Patent Application No. 99850174.6, to support the claim of foreign priority benefits under 35 U.S.C. §119 in connection with the above-identified application.

Respectfully submitted,

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99850174.6

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Wet strength agent and method for production thereof

5 The invention relates to a paper wet strength agent and a method for the production of such an agent. The invention further relates to the production of paper comprising addition of the paper wet strength agent to an aqueous cellulosic suspension and to paper comprising a paper wet strength agent. In addition, the invention relates to the use of a paper wet strength agent as an additive to an aqueous cellulosic suspension.

Background

10 In the papermaking art, wet strength agents like epichlorohydrin-based resins, for example polyaminoamide epichlorohydrin resins have been used for a long time to enhance the strength of paper. Such resins are disclosed in US 3,700,623 and US 3,772,076. The wet strength of a paper relates to its ability to maintain physical integrity and to resist tearing, bursting, and shredding under use, especially under wet conditions. A further important property of wet strengthened paper is the softness, especially for tissue paper or the like. The softness can be described as the tactile sensation perceived when holding or rubbing a paper across the skin.

15 US 5,200,036 discloses a wet strength agent which provides paper with enhanced wet strength. A cationic polyaminoamide epichlorohydrin resin is modified by introduction of a polymerisable unsaturated hydrocarbon moiety thus providing it with ethylenically unsaturated side-chain substituents. The resin is then added to latex-forming monomers whereby co-polymerisation occurs forming bonds between unsaturated polymerisable hydrocarbon moieties of the resin and the latex-forming monomers. The reaction may be assisted by addition of an emulsifier to obtain a desirable suspension of the formed latex particles. Resins of the above-mentioned types are also used as emulsifiers. Usually, the resins are not effective enough when used as a sole emulsifier and these are thus used in combination with an additional compound.

20 US 5,314,721 discloses a process for preparation of vinyl polymer dispersions comprising resin based on a cationic polyaminoamide whose terminal groups have been substituted with long-chain aliphatic hydrocarbon radicals which have at least 7 carbon atoms and are derived from monocarboxylic acids. The product obtained is used as a sizing agent.

25 Although the above epichlorohydrin-based resins in some applications show adequate wet strength and emulsifying properties, it would be desirable to be able to provide further and improved wet strength agents for paper and methods for providing such agents. It would also be desirable to be able to provide wet strength resins and

strength, WS is the wet tensile index and DS is the dry tensile index of a paper. RWS is hence a measure of the softness of a paper; the higher the RWS, the higher the softness of the paper. The present wet strength resins and agents also provide improved emulsifying properties and can be used as sole emulsifiers without additional compounds which may give rise to undesirable foam formation.

The term "wet strength agent", as used herein, refers to an agent capable of imparting better wet strength properties to paper compared to paper containing no such agent. The wet strength agent comprises a wet strength resin. The term "wet strength resin", as used herein, refers to a resin capable of imparting better wet strength properties to paper compared to paper containing no such resin.

The method for the production of a paper wet strength agent comprises a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to provide a nitrogen-containing polymer with hydrophobic side-chain substituents, a second step of reacting the product obtained with a crosslinker to form a wet strength resin, and a third step comprising forming of particles by emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin formed.

Suitably, the nitrogen-containing polymer is a polyaminoamide, a polyamine or other nitrogen-containing polymer. Preferably, a polyaminoamide is used which may constitute the reaction product of a polycarboxylic acid, suitably a dicarboxylic acid, and a polyamine. By the term "carboxylic acid" is meant to include carboxylic derivatives such as anhydrides and esters. Suitable polycarboxylic acids include saturated or unsaturated aliphatic or aromatic dicarboxylic acids. Preferably, the polycarboxylic acids contain less than 10 carbon atoms. Suitable polycarboxylic acids include oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and derivatives thereof. Mixtures of these compounds can also be applied. Suitable polyamines include polyalkylene polyamines, e.g. diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine and the like or mixtures thereof. Further, any polyaminoamide prepared according to a method disclosed in EP 802 215 A1, hereby incorporated by reference, may be used. Suitably, the molecular weight of the nitrogen-containing compound ranges from 100 to 50000, preferably 500 to 10000. Suitably, the polyamine to polycarboxylic acid ratio is 0.49:1 to 1.49:1, preferably less than 1.3:1, e.g. 1.3:1 to 0.7:1. Suitably, diethylenetriamine and adipic acid are reacted to form a polyaminoamide.

Suitably, the hydrophobic compounds used can contain groups of carboxylates or derivatives thereof. The hydrophobation reaction between the nitrogen-containing polymer and the hydrophobic compound can be performed via alkylation, vinyllog addition

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dialkylaminoalkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylates, N,N-dialkylaminoalkyl(meth)acrylates, ethyl chloride, propyl chloride (n-, t-, l-) butyl chloride, pentyl chloride, hexyl chloride, 2-ethylhexyl chloride, octyl chloride, decyl chloride, dodecyl chloride, hexadecyl chloride, octadecyl chloride, ethyl epoxide, propyl epoxide, 5 (n-, t-, l-) butyl epoxides, pentyl epoxide, hexyl epoxide, 2-ethyl-hexyl epoxide, octyl epoxide, decyl epoxide, dodecyl epoxide, hexadecyl epoxide, octadecyl epoxide, ethylene, propylene, (n-, t-, l-) butene, pentene, hexene, 2-ethyl-hexene, octene, decene, dodecene, hexadecene, and octadecene.

Other suitable hydrophobic compounds include substituted succinic anhydrides 10 containing a group selected from alkyl, alkenyl, aralkyl, or aralkenyl, and ketene dimers or multimers. Examples of such compounds are disclosed in WO98/39376, hereby incorporated by reference.

The reaction is suitably carried out in water, neat or in other solvent, e.g. in an organic solvent, e.g. methanol, ethanol or the like, capable of at least partly dissolving the 15 reactants without taking part in the reaction under the reaction conditions. Mixture of such solvents can also be used. The reaction is preferably carried out in water. The molar ratio nitrogen-containing polymer (based on amino mols) to hydrophobic compound can be at least 1:1, suitably 2:1 to 99:1, preferably 3:1 to 40:1. The reaction temperature may range from about 25 °C to about 150 °C, preferably from about 60 to about 90 °C.

20 In a second step, the hydrophobised nitrogen-containing polymers are reacted with a crosslinker. The term crosslinker or crosslinking agent, as used herein, is meant to denote a compound having the ability to crosslink the resin and/or to form bonds to cellulosic fibres. Suitably, the crosslinkers, sometimes referred to as intralinkers in EP 802 215 A1, describing various intralinkers, hereby incorporated by reference, can 25 comprise epihalohydrins e.g. epichlorohydrin; diepoxides, diacrylates, dimethacrylates, diacrylamides, and dimethacrylamides and mixtures or derivatives thereof are used. Preferably, epichlorohydrin is used as crosslinker.

The reaction is suitably carried out in an aqueous solution, neat or by use of other solvent than water, e.g. ethanol, propanol or the like or mixtures thereof. Suitably, 30 the solvent can not react with the reactants under the reaction conditions used. Preferably, the reaction is carried out in water. The reaction temperature may range from about 0 °C to about 150 °C, preferably between from about 4 to about 80 °C. The molar ratio of the hydrophobised nitrogen-containing polymer (based on amino-mols) to crosslinker in the reactant composition may be 10:1 to 1:10, preferably 2:1 to 1:2.

35 In a third step according to the invention, the method comprises emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin as formed after the second step hereabove. The monomers may be

The hydrophobic group of the hydrophobic side-chain can contain up to 40 carbon atoms, preferably 2-18 carbon atoms, most preferably 4-16 carbon atoms.

According to another preferred embodiment of the invention, the side chain can contain 2-11 carbon atoms, preferably 4-10 carbon atoms.

- 5 The hydrophobic side-chain substituents may derive from e.g. (meth)acrylates, alkyl(meth)acrylamides, olefins, esters, ethers, diazo compounds, carboxylic acids, acid anhydrides, alkyl halides including chlorides, bromides and iodides, epoxides, alkyl sulphonates, or alkyl sulphates, or mixtures thereof containing a hydrophobic group.

- Specific examples include substituents derived from  $\alpha$ ,  $\beta$ -unsaturated esters or  
 10 amides like lauryl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, N-alkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylamides, N,N-dialkylaminoalkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylates, N,N-dialkylaminoalkyl(meth)acrylates, alkyl sulphonate, alkyl sulphates, ethyl chloride, propyl chloride (n-, t-, l-) butyl chloride, pentyl chloride, hexyl chloride, 2-ethylhexyl chloride,  
 15 octyl chloride, decyl chloride, dodecyl chloride, hexadecyl chloride, octadecyl chloride, ethyl epoxide, propyl epoxide, (n-, t-, l-) butyl epoxides, pentyl epoxide, hexyl epoxide, 2-ethyl-hexyl epoxide, octyl epoxide, decyl epoxide, dodecyl epoxide, hexadecyl epoxide, octadecyl epoxide, ethylene, propylene, (n-, t-, l-) butene, pentene, hexene, 2-ethyl-hexene, octene, decene, dodecene, hexadecene, and octadecene. Most preferably, the  
 20 hydrophobic side-chains substituents are derived from acrylates as exemplified above.

Other suitable substituents may derive from substituted succinic anhydrides containing a group selected from alkyl, alkenyl, aralkyl, or aralkenyl, and ketene dimers or multimers. Further examples of suitable substituents may be derived from the compounds disclosed in WO98/39376, hereby incorporated by reference.

- 25 A derivative of a crosslinker can be attached to the nitrogen-containing polymer which makes it possible to create bonds to nitrogen-containing polymers and/or cellulosic fibres. Derivatives of a crosslinker can be derived from epihalohydrins e.g. epichlorohydrin, diepoxides, diacrylates, dimethacrylates, diacrylamides, and dimethacrylamides or mixtures or derivatives thereof may be used. Preferably, the  
 30 crosslinker is derived from epichlorohydrin.

- According to one preferred embodiment, the cationic nitrogen-containing polymer is either a polyaminoamide-epichlorohydrin resin or a polyamine-epichlorohydrin resin having saturated hydrophobic side-chains. Suitably, at least 10 % and preferably up to about 100 % of the nitrogen atoms of the cationic resin comprise cationic groups.  
 35 Suitably, up to 100 % of the nitrogen atoms of the resin comprise hydrophobic groups, preferably up to 50%, most preferably 5-30 %. Suitably, the wet strength agent comprise a composition of polymeric particles and a wet strength resin dissolved in a solvent,

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Example 1

Reaction of a polyaminoamide (PAIM) (produced from adipic acid and diethylene triamine) with a hydrophobic compound (vinyllog addition): 240 g (0.60 amino-mol equivalents) PAIM (53 % solution in water) and 27.3 g (0.15 mol) 2-ethylhexyl acrylate (2-EHAc): were heated for 6 h and 30 min at 80 °C. Subsequently, 176 g of water was added and the solution was cooled down to room temperature. Conversion of acrylate was : 99.7 %.

307 g of the above hydrophobised PAIM solution was reacted with 30 ml epichlorohydrine (ECH) at 6 °C for 6 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached whereupon 155 ml of water was added and the temperature was adjusted to 65 °C to let the viscosity reach 120 mPa s. The reaction was finalised by adding 11 ml of sulfuric acid (50 %) adjusting the pH to 3.5.

Emulsion polymerisation: The ratio resin to styrene was 1:2.

A solution of 47 g of the above produced wet strength resin, 104 g water and 1.5 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was then increased to 50°C whereupon 0.5 g Wako VA 044 and 1 ml styrene were added to the solution. 10 min later, additional styrene was added (total amount: 25 g). After 5 h at 50 °C, the temperature was increased to 70 °C at which temperature the solution was kept for an hour.

Example 2

Reaction of Polyaminoamide (PAIM) with a 2-ethylhexylacrylate (2-EHAc) (vinyllog addition): 82 g (0.20 amino-mol equivalent) PAIM (52 % solution in water), 1.84 g (0.01 mol) 2-ethylhexyl acrylate (2-EHAc) and 43 g of water were heated for 2 h at 80 °C. Conversion of acrylate: 98.9 %.

15,4 ml epichlorohydrine (ECH) was added to 125 g of the above hydrophobised PAIM solution at 6 °C for 6 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased to 65 °C and a viscosity of 120 mPa s was reached whereupon 86 ml of water was added. The temperature was raised to 65 °C and kept at 65 °C until the viscosity reached 120 mPa s. The reaction was finalised by addition of 11 ml sulfuric acid (50 %) adjusting the pH to 3.5.

Emulsion polymerisation: The resin/styrene ratio was 1:0.5. A solution of 88.5 g of the above wet strength resin , 92 g water and 1.5 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 45 °C. 0.04 g Wako VA 044 and 2 ml styrene were added whereafter the temperature was raised to 50 °C. After 10



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amount: 17 g). After 3 h at 50 °C the reaction mixture was cooled down to room temperature.

#### Example 6

- 5 25 % 2-ethylhexyl acrylate was used to hydrophobise PAIM. A monomer mixture of styrene with t-butyl acrylate (0.45 : 0.05) was used. Emulsion polymerisation: A solution of 121 g of the wet strength resin of example 1 (solids 28 %), 131 g of water and 1 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 45°C. 0.04 g Wako VA 044 and 2 ml of a monomer mixture (styrene : t-butyl
- 10 acrylate = 0.45 : 0.05) were then added and the temperature was raised to 50 °C in 10 min. Subsequently, the monomer mixture was added (total amount: 17.0 g). After 3 h at 50 °C the reaction mixture was cooled down to room temperature.

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#### Application Testing

- Paper sheets were prepared on the dynamic sheet former "Formette". The furnish consisted of 35 % CTMP and 65 % TCF refined to 25° SR. Grammage was 55 g/m<sup>2</sup>. The paper was artificially cured 10 min at 105 °C before conditioning the paper according to DIN 5312. Tensile testing was done as described in DIN 53112. For wet
- 20 tensile testing the paper was soaked 60 min at room temperature. For comparison reason data on paper prepared by using a conventional polyaminoamide epichlorohydrin resin, is given, too.

Sample	Dry tensile index in Nm/g	Wet tensile index in Nm/g	Relative wet strength in %
Conventional resin	49	13	27
Example 1 Wet Strength Resin	44	12	27
Example 1 Wet Strength Emulsion	37	14	37
Example 2 Wet Strength Resin	50	13	26
Example 2 Wet Strength Emulsion	51	15	30
Example 3 Wet Strength Resin	37	12	32

Claims

1. Method for preparing a wet strength agent characterised in that it comprises a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to form hydrophobic side-chain substituents on the polymer, a second step of reacting the hydrophobised nitrogen-containing polymer obtained with a crosslinker to form a cationic nitrogen-containing resin, and a third step comprising forming of particles by emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin formed.
2. Method according to claim 1 characterised in that the nitrogen-containing polymer is a polyamine or a polyaminoamide.
3. Method according to any of the claims 1-2 characterised in that the first step is a vinyllog addition or alkylation where the hydrophobic compound is selected from alkyl sulphonates, alkyl sulphates, epoxides, olefins, diazo compounds, ethers, or alkyl halides, or mixtures thereof.
4. Method according to any of claims 1-3 characterised in that the hydrophobic compounds comprise a hydrophobic chain having 2-18 carbon atoms.
5. Method according to any of claims 1-4 characterised in that the hydrophobic compounds comprise a hydrophobic chain having 4-16 carbon atoms.
6. Method according to any of claims 1-5 characterised in that the hydrophobic compound contains a chain of atoms containing at least one hetero atom.
7. Method according to any of claims 1-6 characterised in that the crosslinker is epichlorohydrin.
8. Method according to any of the claims 1-7 characterised in that the monomers are selected from styrene, butadiene, alkyl (meth)acrylates, alkyl(meth)amides, (meth)acrylonitrile, vinyl acetate, or vinyl amide, or mixtures or derivatives thereof.
9. Method as claimed in any of claims 1-8 characterised in that the hydrophobic compound is a saturated compound, or an unsaturated compound, resulting in a nitrogen-containing polymer having saturated side-chain substituents.
10. Paper wet strength agent obtainable by a method as defined in claim 9.
11. Paper wet strength agent characterised in that it comprises a wet strength resin comprising cationic nitrogen-containing polymers having hydrophobic saturated side-chain substituents and groups derived from a crosslinker; and polymeric particles.
12. Paper wet strength agent according to claim 11 characterised in that the hydrophobic side-chain substituents contain a hydrophobic group attached to a

Abstract

The invention relates to a method for preparing a wet strength agent comprising a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to form hydrophobic side-chain substituents on the polymer, a second step of reacting the hydrophobised nitrogen-containing polymer obtained with a crosslinker to form a cationic nitrogen-containing resin, and a third step comprising forming of particles by emulsion polymerisation of one or more ethylenically unsaturated monomers in the presence of the wet strength resin formed. The invention further relates to a wet strength agent and resin.

10 It further relates to the use of said agent and resin in cellulosic suspensions, the production of paper, and paper comprising said agent and resin.



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nitrogen atom of the nitrogen-containing polymer via a chain of atoms comprising 2-18 carbon atoms.

13. Paper wet strength agent according to any of claims 11-12 characterised in that the hydrophobic side-chain substituents are selected from derivatives of alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, alkyl halides, epoxides, or olefins, or mixtures thereof.

14. Method for preparing a wet strength resin characterised in that it comprises a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to form hydrophobic side-chain substituents, in which said hydrophobic compound is selected from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, olefins, diazo compounds, ethers, alkyl halides, or epoxides or mixtures thereof, and a second step of reacting the hydrophobised nitrogen-containing polymer obtained with a crosslinker to form a cationic nitrogen-containing resin.

15. Method according to claim 14 characterised in that the hydrocarbon compound contains 4-16 carbon atoms.

16. Paper wet strength resin obtainable by a method as defined in any of claims 14-15.

17. Paper wet strength resin characterised in that the resin comprises cationic nitrogen-containing polymers having saturated hydrophobic side-chain substituents selected from compounds derived from alkyl(meth)acrylates, alkyl(meth)acrylamides, alkyl sulphonates, alkyl sulphates, olefins, alkyl halides, or epoxides or mixtures thereof, and groups derived from a crosslinker.

18. Process for production of paper according to any of the preceding claims comprising addition of a paper wet strength resin or agent to an aqueous cellulosic suspension.

19. Paper comprising a paper wet strength resin or agent according to any of claims 1-18.

20. Use of a paper wet strength agent or resin according to any of the claims 1-19 for the production of paper.

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Example 3 Wet Strength Emulsion	37	13	34
Example 4 Wet Strength Emulsion	33	12	36
Example 5 Wet Strength Emulsion	35	11	31
Example 6 Wet Strength Emulsion	37	12	33

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minutes, additional styrene was added (total amount: 12 g). After 3 h at 50 °C, the reaction mixture was cooled down to room temperature.

### Example 3

5           260 g (0.65 amino-mol equivalent) PAIM (53 % solution in water) (Polyaminoamide, PAIM) and 25% 41.0 g (0.16 mol) dodecyl acrylate (vinyllog addition) were heated for 4 h 30 min at 80 °C. Subsequently, 211 g water was added whereafter the mixture was cooled down to room temperature.

10           302 g of the above hydrophobised PAIM was then reacted with 30 ml (0.20 mol) epichlorohydrine (ECH) at 6 °C for 4 min. Subsequently, the temperature was increased until 20 °C was reached. The temperature was then increased until 50 °C and a viscosity of 120 mPa s was reached. 185 ml water was then added and the temperature was raised to 65 °C and kept at that temperature until the viscosity reached 120 mPa s. The reaction was finalised by addition of 10 ml sulfuric acid (50 %) adjusting the pH to 3.5.

15           Emulsion polymerisation: The resin/styrene ratio was 1 : 1. A solution of 75.0 g of the above wet strength resin, 100 ml water and 1 ml defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 50°C whereupon 30 mg Wako VA 044 and 1 ml styrene were added. After 10 minutes, additional styrene was added (total amount: 20.5 g). After 5 h at 50 °C, the temperature was increased to 70 °C  
20           and set at that temperature for one hour.

### Example 4

          In the emulsion polymerisation, butyl acrylate was used instead of styrene. A solution of 75.0 g of the wet strength resin of example 3 (13 % solids), and 1.5 g  
25           defoamer (10 % solution in water) was purged with nitrogen. The temperature was increased to 45°C. 0.03 g Wako VA 044 and 2 ml butyl acrylate were then added whereupon the temperature was increased to 50 °C. After ten minutes, styrene was added (total amount: 14.2 ml). After 2 h 50 min at 50 °C, the temperature was increased to 70 °C which temperature was kept for one hour.

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### Example 5

          25 % 2-ethylhexyl acrylate was used to hydrophobise PAIM. Emulsion polymerisation: A solution of 121 g of the wet strength resin of example 1 (solids 28 %), 131 g water and 1 ml defoamer (10 % solution in water) was purged with nitrogen. The  
35           temperature was increased to 45°C. 0.04 g Wako VA 044 and 2 ml of a monomer mixture (styrene: 1,6-hexandiol diacrylate = 0.375 : .125) were added whereupon the temperature was raised to 50 °C in 10 min. Subsequently, the monomer mixture was added (total

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preferably the wet strength agent comprise an aqueous composition. Suitably, the aqueous composition has a solid content of 5-50 weight percent.

The invention further relates to a wet strength resin as above described.

The invention also relates to the use of the paper wet strength resin and agent,

5 as described above for the production of paper. The use comprises addition of the resin or agent to an aqueous suspension containing cellulosic fibres. The amount of resin added to dry cellulosic fibres may be in any proportions, preferably 0.1-50 kg/tonne dry cellulosic fibres. The paper wet strength resin and agent are preferably produced as aqueous dispersions which comprise the resin, water and optionally emulsified particles.

10 The dispersion can then be added to an aqueous cellulosic suspension to treat paper-forming cellulosic fibres. The paper wet strength resin and agent may also be added to the produced paper and thus providing surface treatment of the paper. Further, the addition of the wet strength resin or agent may be added together with any other chemical known in the art conventionally used in the production of paper, e.g. sizing agents, softeners, retention aids, dewatering agents, dry strength agents, charge control agents or any other conventional chemicals, e.g. guar, carboxymethyl cellulose, polyacrylamide, polystyrene. Further, conventional fillers can be added thereto, e.g. clay, calcium carbonate, titanium dioxide, talc, aluminium silicate, calcium sulphate, calcium silicate or others described in WO 97/37080. Further, the wet strength agent may be

20 added to the cellulosic fibre-containing suspension in any proportion. Before the wet strength resin or agent are added to an aqueous cellulosic suspension, the aqueous dispersion containing the resin or agent may be subjected to removal of toxic by-products by means of ion exchange, electrodialysis, enzymatical treatment, filtration, steam stripping or the like in order not to add any toxic products, e.g. chloropropanol, dichloropropanol to the cellulosic suspension. These methods are further described in for example EP 666 242 A1, EP 510 987 A1 and WO 92/22601. The invention also relates to the production of paper comprising addition of a paper wet strength resin and/or an agent as described hereabove to an aqueous cellulosic suspension. The invention also relates to paper comprising a wet strength resin and/or an agent as described hereabove.

30 The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the gist and scope of the present invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the claims. While the examples herebelow provide more specific details of the reactions, the following general principles may here be disclosed. The following examples will further illustrate how the described invention may be performed without limiting the scope of it.

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selected from styrene, butadiene, vinyl acetate, vinyl amide, alkyl(meth)acrylamide, alkyl(meth)acrylate, e.g. methyl (meth)acrylate, butyl (meth)acrylate, butyl glycidyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, dodecyl(meth)acrylate, octadecyl(meth)acrylate; (meth)acrylonitrile, isoprene, or 1,6-hexandiol diacrylate, or

- 5 mixtures or derivatives thereof. As a result of the polymerisation process, the formed wet strength resin can be anchored to the polymeric particles formed yielding a wet strength agent. As initiator of the polymerisation reaction, any conventional initiator can be used. For example, Wako VA 044 can be used. Preferably, the initiator is water soluble. In the emulsion polymerisation reaction, the wet strength resin works as an emulsifier during the
- 10 particle formation. The formed particle may be composed of one sole or a mixture of unsaturated ethylenically polymerisable monomers as above exemplified. The reaction is preferably carried out in water, organic solvents, e.g. ethanol, propanol or the like, or mixtures of organic solvents or mixtures of both water and organic solvents. The reaction temperature may range from 4 °C to about 150 °C, preferably from about 30 to about 90
- 15 °C. The weight ratio resin to monomer can be 100:1 to 1:100, suitably 10:1 to 1:50.

The invention further relates to a method for preparing a wet strength resin comprising the first and second steps of the method as above described.

- The invention also relates to a wet strength agent comprising polymeric particles and a wet strength resin comprising a cationic nitrogen-containing polymer having
- 20 saturated hydrophobic side-chain substituents and a derivative of a crosslinker.

The polymeric particles can be formed from polymerised monomers as described above. Preferably, monomers are selected from styrene, acrylates and mixtures or derivatives thereof.

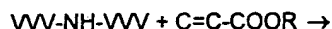
- The cationic nitrogen-containing polymer has saturated hydrophobic side-chain
- 25 substituents and derivatives of a crosslinker attached to the nitrogen atoms of the polymer.

- Examples of suitable nitrogen-containing polymers include well-known available commercial products which may be prepared as described above or according to conventional methods known in the art. Examples of suitable nitrogen-containing
- 30 polymers include polyaminoamides, alkyl polyamines, polyimines, and polyvinylamines.

- Hydrophobic saturated side-chain substituents are attached to the nitrogen atoms of the nitrogen-containing polymer. The term hydrophobic side-chain substituent is here meant to include hydrophobic groups containing e.g. hydrophobic linear or branched hydrocarbon chains which can be linked, e.g. via a hetero atom by a covalent bond, to a
- 35 nitrogen atom of the nitrogen-containing polymer. Hydrophobic groups may also include cyclic chains including cyclic hydrocarbons. Combinations of linear, branched and cyclic hydrocarbons are also included in the concept of hydrophobic groups.

4

or other reaction. The vinyllog addition may be illustrated by the following schematic reaction:



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wherein VV-NH-VV represents a section of the nitrogen-containing polymer,

15 C=C-COOR represents a hydrophobic compound containing a vinyl group. The vinyl group, i.e. the C=C group, of the hydrophobic compound can react with the nitrogen atoms of the polymer. R stands for a hydrophobic group of the hydrophobic compound which may be an alkyl, alkenyl, aryl, cycloalkyl or cycloalkenyl group. In case the vinyllog reaction is applicable, the unsaturation of the vinyl group of the hydrophobic compound is  
20 consumed after having reacted with a nitrogen atom of the polymer.

According to one preferred embodiment, the hydrophobic compound is a saturated compound, or an unsaturated compound, resulting in a nitrogen-containing polymer having saturated side-chain substituents.

25 The hydrophobic compounds can contain a hydrophobic group of up to 40 carbons, preferably 2-18 carbons, most preferably 4-16 carbons.

According to another preferred embodiment of the invention, the hydrophobic compound can contain 2-11 carbons, preferably 4-10 carbons.

30 The hydrophobic chains of the hydrophobic compounds can be attached to the nitrogen-containing polymer via a chain of atoms, which can contain at least one hetero atom, via a covalent bond.

The hydrophobic compound may be selected from (meth)acrylates, alkenyl(meth)acrylate, alkyl(meth)acrylamides, olefins, esters, ethers, diazo compounds, carboxylic acids, acid anhydrides, alkyl halides including chlorides, bromides and iodides; epoxides, alkyl sulphonates, alkyl sulphates and mixtures or derivatives thereof  
35 containing a hydrophobic group. Examples suitably include  $\alpha$ ,  $\beta$ -unsaturated esters or amides like lauryl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, N-alkyl(meth)acrylamides, N-alkylaminoalkyl(meth)acrylamides, N,N-

agents exhibiting improved softness properties. Further, it would be desirable to be able to provide further resins having improved emulsifying properties.

#### The Invention

5 According to the present invention, it has been found that further and improved wet strength agents for paper can be obtained by a composition containing polymeric particles and hydrophobic hydrocarbon groups providing side-chain substituents on wet strength resins. It has also been found a new method for the production of such wet strength resins and agents. It has further been discovered that the wet strength agents  
10 and resins produced by the method according to the present invention give paper improved softness properties.

More specifically, the invention relates to paper wet strength agents comprising polymeric particles and wet strength resins comprising a cationic nitrogen-containing polymer having hydrophobic side-chain substituents. The invention further relates to a  
15 method for the production of a paper wet strength agent comprising a first step of reacting a nitrogen-containing polymer with a hydrophobic compound to provide a nitrogen-containing polymer with hydrophobic side-chain substituents, a second step of reacting the product obtained with a crosslinker to form a cationic wet strength resin, and a third step comprising emulsion polymerisation of one or more ethylenically unsaturated  
20 monomers in the presence of the wet strength resin formed. Further, the invention relates to a paper wet strength agent obtainable from the method above. The invention further relates to a new wet strength resin and a method for preparing a wet strength resin according to the two first steps as described hereabove. The invention also relates to the production of paper comprising addition of a paper wet strength resin or agent to a  
25 cellulosic suspension and to the use of a paper wet strength resin or agent for the production of paper. The invention also relates to paper comprising paper wet strength resins and agents. The invention is further defined in the appended claims.

The present invention provides resins and agents having the ability to impart improved wet strength properties to paper. The invention further provides a simple,  
30 convenient and effective synthetic route for the preparation of wet strength resins and agents. Thereby, the wet strength resins and agents of this invention can be prepared in high yield.

The present invention also provides wet strength resins and agents which make it possible to produce paper having enhanced softness properties. The softness of a  
35 paper sheet can be estimated by means of the relative wet strength value, which is defined as the ratio between the wet tensile index and the dry tensile index according to the formula  $RWS \text{ (in \%)} = (WS/DS) \cdot 100$ , where RWS stands for the relative wet